Two-dimensional Crystallization of Silica nanospheres using Coplanar DC Electric field

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Abstract

Two-dimensional crystal has been achieved and controlled with the aid of DC electric field applied between two electrodes at 5 millimeters separating distance between them. Sol-gel method has been used to prepared nanosilica particle which used in this work as well as TiO2 nanopaowder. The assembly of the silica particles is due to the interaction between the electrical force, the particles dipole, and the interaction between the particles themselves. When a DC voltage is applied, the particles accumulated and crystallized on the surface between the electrodes. The Light diffraction demonstrates that the hexagonal crystal is always oriented with one axis along the direction of the field. The particles disassemble when the field is turned off, and the process can be repeated many times. The diffraction patterns from all consecutively formed crystals are identical. This assembly is driven by forces that depend on the electric field gradient; the process can be controlled via the external field strength, and the viscosity of the liquid media.

Keywords

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تكوين بلورة ثنائية الأبعاد من جسيمات السيليكا بتاثير المجال الكهربائي

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الخلاصة

تم الحصول على بلورة ثنائية الأبعاد من جسيمات السيليكا و التحكم بها بواسطة مجال كهربائي مسلط بين قطبين المسافة بينهما 5 مليمتر. تم تحضير جسيمات السيليكا المستخدمة في هذا العمل باستخدام تقنية السول–جل ،وكذلك تم استخدام مادة ثنائي اوكسيد التيتانيوم . هذا التجميع هو نتيجة التفاعل بين القوة الكهربائية وثنائيات القطب المتكونة من الجسيمات وكذلك التفاعل بين ثنائيات الأقطاب نفسها . عند تسليط الفولتية المستمرة تتجمع الجسيمات على السطح بين القطبين الكهربائيين .نمط الحيود الضوئي خلال لبلورة المتكونة يشير إلى الترتيب السداسي للجسيمات خلال البلورة بين القطبين . عند إزالة المجال الكهربائي تعود الجسيمات لحلة عدم التجمع وهذه العملية يمكن أعادتها عدة مرات . يمكن الحصول على نفس نمط الحيود من كافة مناطق البلورة . هذه العملية يمكن التحكم بها بواسطة قوة المجال الكهربائي وكذلك لزوجة السائل المستخدم.

Introduction

The engineered assembly of colloidal particles can be used to create colloidal

crystals that serve as precursors for advanced materials for photonics' could be used in sensors, displays, and optical or electronic devices[1]. Colloidal crystal assembly can be effected by a variety of forces such as electrostatic repulsion and Vander Waals attraction, hydr-odynamic liquid drag [2] and capillary forces acting on fluid surfaces [3]. In most situations, however, these forces do not readily provide the specific control and rapidity required for technological app-lications of particle assembly processes[5] .An efficient and convenient way to manipulate colloidal particles in suspension is to apply electrical fields from external electrodes. Processes driven by external fields can be rapid and precisely controlled. Electrophoretic forces make charged particles move in a constant (DC) field, and they can be studied and used [4]. Electrical fields can be used to speed up the assembly of colloidal crystals. Both DC and AC electric fields have been used to drive the formation of two-dimensional (2D) and three- dimensional (3D) colloidal crystals between opposing par-allel electrodes [5].

Electrophoretic attraction of particles to surfaces has been used to speed the assembly of 3D crystals in order to make microsphere "opals". The application of DC fields in the thin gap between conductive electrodes has been demonstrated to be a rapid and efficient way to assemble 2D crystals on surfaces [4]. Driving force bringing the particles together in these two- dimensional crystals and has been experimentally and theoretically proven to be the electrohydrodynamic interaction of the flows around the microspheres, leading to att-raction between the particles and their aggregation into ordered arrays [6]. AC fields have also been used to modulate and align the structure of colloidal crystals. The chaining effect has been used to induce annealing and large-scale orientation of coll-oidal crystals formed by conventional sedimentation. When the opposing electrodes areas separate only a few particle diameters away from each other, the spheres are confined in a film. The repulsion between the parallel dipoles induced in the particles leads to long-range repulsive forces and 2D crystallization [5].

Here, we report the joint between the dipole—field (DEP) and dipole—dipole (chaining) interactions for the assembly of colloidal microspheres into one-dimensional (1D) and two-dimensional structures on the glass surface of a thin cell. The geometry of this cell is unique in which it has both electrodes deposited on the same surface with a large gap between them. Thus, the electric field is parallel, and the gradient of the field is normal, to the surface.

1. Mechanism of Crystal Assembly.

Crystal assembly can be readily explained in terms of a combination of the two types of DC-field-driven forces intr-oduced above[8]. Schematics of the two stages of the process are presented in (Figure1). The first, faster stage is the formation of particle chains because of attractive dipolar interparticle interactions (Figure1-a). In the second and slower stage of the crystallization process, the particles and particle chains are attracted to the region of maximum field intensity, which for this geometry is on the surface of the glass slide between the planar electrodes (Figure 1-b). The 2D crystal structure then forms on the surface of the slide due to lateral interactions between the dipoles in the adjacent particle chains.

This role for the gradient-dependent DEP forces outlines a major difference between the coplanar electrode systems studied here and the plane-parallel electrode configurations studied previously [4]. The role of the DEP attraction and confinement was verified in experiments in which the cell was rotated 180° so that the electrodes were above the colloidal suspension. In this case, the dielectrophoretic force moves the microspheres upward against gravity and they assemble on the top surface [8].

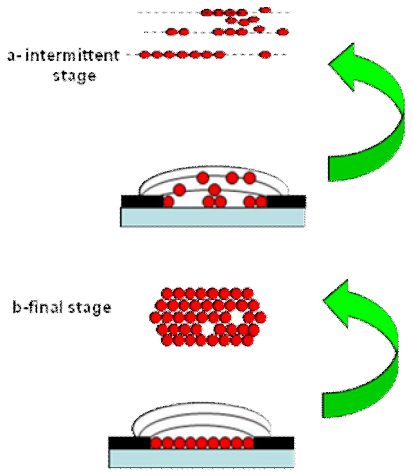


Figure 1 Schematics of the two stages of the process of crystallization

The kinetics of the assembly process and the diffraction pattern remain unaltered, so the DEP force is the major factor confining particles on the surface. The combination of dipole—dipole chaining and dipole— field gradient forces also explains the specific orientation of the crystal. The assembly of the particles into 1D chain parallel to the direction of the electric field determines the overall orientation of the crystal formed after the chains are crystallized on the glass surface[7].

This, together with the strong in-plane alignment of the arrays because of DEP attraction, sets all of the geometrical parameters of the crystal, which in turn gives the excellent alignment and the consistently predictable position of the diffraction spots.

The process of 2D crystal disassembly in less than a second is remarkably fast compared to the slow relaxation of the structure in most 3D crystals. Disassembly is driven by the Brownian motion of the particles after they are released by the field and accords with diffusion perpendicular to the plane of the substrate, in which direction the particles are not constrained by others in the 2D crystal. Precise calculations of the relaxation times of this process are complex, because they need to take into account the opposing forces of diffusion and gravitational sedimentation.

The relative importance of the Brownian and gravitational forces to the particle flux can be evaluated by the Peclet number $P_e = hU/D$, where h is the characteristic displacement (assumed to be of the order of the particle diameter), U is the sedimentation velocity, and D is the particle diffusion coefficient. The sedimentation velocity and diffusion coefficient of a particle of radius r are given by $U = 2\Delta\rho gr2/9\mu$ and $D = kT/ 6\pi\mu r$, where $\Delta\rho$ is the difference in the densities, g is the gravitational acceleration, μ is the viscosity, and kT is the Boltzmann constant multiplied by the temperature [5].

Experimental part

1. Materials

The following material have been used in this work; tetraethylorthosilicat (TEOS) precursor Si $(O\text{-}C_2H_5)_4$ purity > 99% used without any farther purification, Deionized water, ethanol alcohol absolute grad and NH_3OH ammonia solution

2. Samples preparation

2.1 Slide preparation

Two planar Aluminum electrodes were deposited on high cleaned slide using thermal deposition method. The thickness of the Aluminum coating is 100 nm. These two electrodes were covered by silica coating using spin coating technique to protect the aluminum thin films. Further 0.1 mm silica glass used as spacer on the aluminum films. Thus there was a gap between these two silicon slides, where the particles take place into this gap .Two wires has been connected to the electrodes using liquid solder for high voltage connection.

2.2. Colloidal particles preparation

Using sol gel method, colloidal silica particles were prepared. Two solutions were prepared: silica solution 1 ml of tetraethylorthosilicat (TEOS) and 2 ml of ethanol were mixed. The mixture were denoted as sol I. Catalyst solution was prepared containing 2ml of water (catalyzed by NH3 gives PH 13) and 2 ml of ethanol .

The resultant mixture was denoted as sol II. The catalyst solution was slowly adding to the silica solution with stirring. The mixture was powered into an appropriate mold, and then kept at 40 C^{o}. The sample was appeared as participate powder which represent a silica colloidal particles.

3. Experimental setup

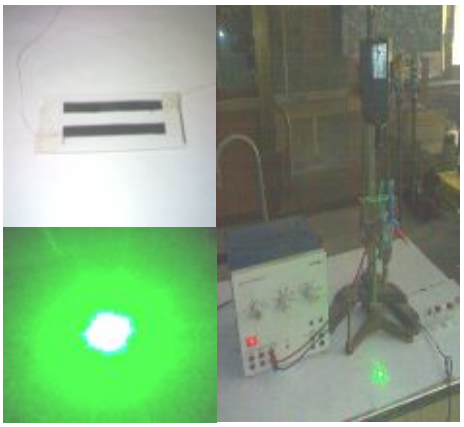
A schematic illustration of the setup is shown in Figure (2-a). Particle assembly takes place inside a thin layer of suspension encapsulated above a microscope glass slide (25 x 75 mm plain microslide, VWR Scientific, PA). The particle suspension was placed in the gap between the electrodes on the glass surface and was enclosed inside a hydrophobic spacer (PAP Pen, Inno Genex, CA) and covered with a microscope glass cover slip (25 x 25mm micro cover glass). The characteristic dimensions of the experimental cell are given in the inset of Figure (2-b). The concentration of the particles inside the cell was adjusted with respect to the thickness, so when all of the particles from the cell volume were collected on the surface they formed a complete closely packed monolayer. The diffraction pattern of a green laser beam (λ = 531.5 nm), beam diameter = 2 mm, was collected on a screen 30 cm below the glass slide. The diffraction patterns were recorded using a digital camera.

Results and Discussion

(Figure 3) shows the laser diffraction pattern obtained from the 531.5 laser beam as a function of the time after the electric field have been applied. Before the field is applied, the particles are randomly distributed through the volume of the cell due to Brownian motion and display diffuse scattering only see Figure (3-a).

While figure (3-b) shows an intermediate stage as the pattern evolves into hexagonal of six spots after approximately 1 min of applied electric field. This spot is indicative of diffraction from hexagonally close-packed spheres. The pattern is highly reproducible over the crystal area with the position of the pattern remaining the same, no matter what area of the cell through which the laser is directed . This proves that the crystal has continuous single-domain orientation throughout the whole area as shown in (figure 3-c).

In contrast, the multidomain 2D crystals deposited by conv-entional convective assembly [3] display a ring-line diffraction pattern when the beam size is larger than the characteristic domain size or six spots at different radial positions when scanned with a beam of very small diameter After the electric field is removed, the diffuse scattering pattern is recovered. The diffraction pattern is recovered with the same orientation every time the field is turned on again.



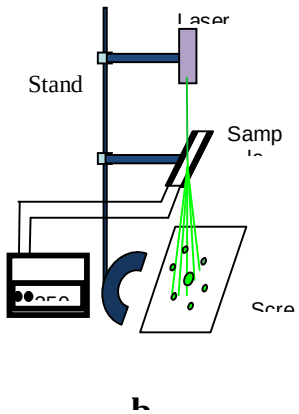


Figure2. Schematics of the experimental

The evolution of the diffraction pattern indicates that two stages are involved in

the assembly of the colloidal crystal. Before the field is applied, it is difficult to obtain a clear image of the particles because they are distributed vertically through the cell and exhibit Brownian motion. Within 20 s of applying the field, the silica spheres align into chains due to the attractive interactions between the induced dipoles.

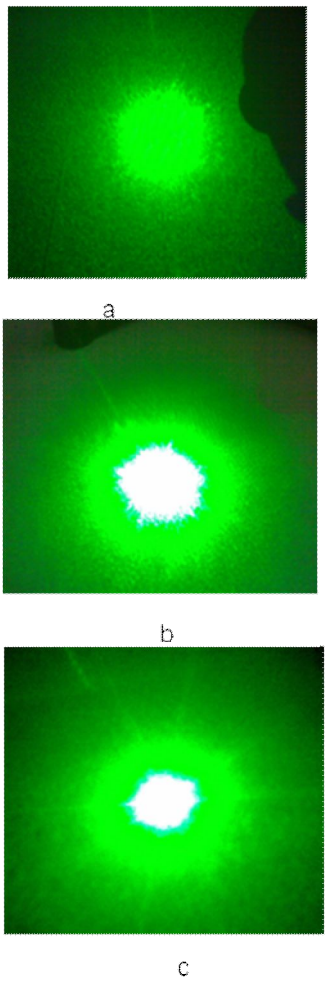


Figure 3 shows the laser diffraction pattern obtained from 2mm diameter spheres as a function of the time

The chains are parallel to the direction of the applied field and thus are perpendicular to the gap between the two planar electrodes (Figure 3a). As more particle chains are collected in the region of maximum field intensity on the surface of the slide. Lateral interactions between the chains result in the formation of a hexagonally 2D close- packed (Figure 3b).

The crystal ultimately consists of a continuous single ordered domain that covers the area of the cell, which is approximately 25 mm^2. This domain size is 2- orders of magnitude larger than that of crystals formed by electrostatic repulsion or by convective assembly onto solid surfaces [5]. The crystal also has a specific orientation, with one axis aligned parallel to the direction of the applied field. Crystals of the same orientation are assembled every time the field is reapplied.

The crystal contains some defects due to impurities or to scratches on the cell, and there are some vacant areas if the particle concentration is not enough to form a complete monolayer, so the diffraction pattern of six spots appeared assembling together i.e. the middle area among the spots becomes bright in time it must be dark [5].

1. Effect of Particle Size and Electrolyte Concentration.

As expected for scattering from hexagonally close-packed spheres, the angle of diffraction depends on the size of the particles in the array. The diffraction angle (θ) in scattering from a 2D array is related to the lattice spacing (h) via the von Laue equation:

$$h = \frac{n\lambda_c}{\sin\theta} \qquad \text{----------(1)}$$

where n is an integer equal to 1 for the diffraction spots nearest to the beam, and λ_c is the wavelength of the laser beam corrected for the refractive indices of the composite media in the scattering environment. λ_c is calculated from the wavelength of the laser in air, λ_o, and the composite refractive index of the media:

$$\lambda_c = \frac{\lambda_0}{(\phi n_p^{\,2} + (1-\phi) n_w^{\,2})^{1/2}} \qquad \text{----------(2)}$$

where ϕ is the volume fraction of particles in a monolayer, and n_p and n_w, are the refractive indices of latex particles and water, respectively. The diffraction angle is also corrected for refraction of the laser beam as it exits the cell using Snell's law.

Subtracting the particle diameter from the calculated center-to-center spacing yields the distance between the surfaces of the particles, and this distance depends on the concentration of electrolyte in the aqueous phase. This is due to repulsive electrostatic interactions between the negatively charged sulfate groups on the latex surfaces. As the concentration of electrolyte in the surrounding media is increased, these interactions are suppresse.

Exact calculations of the effect of electrolyte are complex and require additional data on particle charge as a function of electrolyte and electric potential. Alternatively, the DEP crystallization method offers a possible way to study long-range mul-tibody particle interactions in ensembles by simple laser diffraction [5].

2. Effect of Media Viscosity and Dielectric Permittivity.

The lateral interactions between induced dipoles in the 1D chains can be suppressed by addition of glycerol to the aqueous continuous phase .the six-spot diffraction pattern does not appear even after the field is applied for several minutes, so the addition of glycerol to the media in effect opens a new "chain-only" region of the phase transition diagram.

Addition of glycerol to the continuous phase simultaneously increases the viscosity and decreases the dielectric permittivity of the medium. Therefore, medium viscosity plays a key role, perhaps by suppressing counter ion mobility and therefore modulating the dipolar and dielectrophoretic interactions. This concept has not yet been developed quantitatively.

Conclusions

The solution arrangement is driven by a combination of two complementary forces arising from the interaction of the dipoles induced in the particles with the field that induces them and interactions between the dipoles themselves (dipole—dipole interactions). The crystalline of the particles can be conveniently studied by diff-raction of a laser beam passing through the thin cell. The speed of alignment of the two-dimensional crystallization nan-ospheres is directly proportional to the electric field strength, and inversely proportional to the viscosity of the liquid media. The media viscosity is determined by threshold point above it the particles cannot be crystallized. The six spots can be appeared individually only when the ground slide has perfect purity (without any scratches on the slide), and the number of the particles enough to construct monolayer on the cell.

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